

AQUEOUS BUFFERED FLUORIDE-CONTAINING ETCH RESIDUE
REMOVERS AND CLEANERS

5 CROSS-REFERENCE TO RELATED APPLICATIONS[NOT APPLICABLE]

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR
DEVELOPMENT[NOT APPLICABLE]

10 BACKGROUND OF THE INVENTION

The invention relates to aqueous, buffered fluoride containing compositions having a pH of from greater than 7.0 to about 11.0. These composition are used as resist and etch or ash residue removers and cleaners in the production of semiconductor devices. The buffered, fluoride containing compositions resist changes in pH and exhibit low corrosive effects on metal films such as aluminum, copper, titanium, tungsten and the like, and low oxide etch rates. More particularly the invention relates to aqueous, buffered, fluoride containing compositions useful as resist and etch or ash residue removers and cleaners that use molecules not typically viewed as buffers. The buffers of the present invention include the use of a variety of weak acids or protonated bases which act as weak acids in solution that are effective over a pH range of greater than 7.0 to about 11.0. The invention also includes methods of preparing the fluoride containing compositions and their use.

There are a number of fluoride containing compositions disclosed in the art. Torii (US 5,972,862) discloses fluoride containing compositions used as stripper-cleaners. Tanabe (US 5,792,274 and 5,905,063) disclose resist remover compositions having a pH of from 5 to 8, containing metal-free salts of HF, a water soluble organic solvent, and optionally a corrosion inhibitor. Maruyama (US 5,692,385) discloses a composition containing from 0.1 wt% to 10 wt% ammonium and alkyl ammonium salts of HF, from 72 wt% to 80 wt% of an

organic solvent that is water soluble and the remainder water. According to the teachings in Maruyama both the fluoride containing compound and the solvent must be present in the given ranges, otherwise the detrimental side effects such as corroding of substrates and poor performance occur. None of the above
5 cited references recognize the effective use of buffers to improve the pH stability of fluoride containing compositions.

BRIEF SUMMARY OF THE INVENTION

10 A potential negative attribute of acidic fluoride containing compositions is the oxide etch rate. If the oxide etch rate is too high the fluoride containing compositions have a limited application for via cleaning since critical dimension control may not be adequate. Raising the pH will usually reduce the oxide etch rate. For instance it has been shown that raising the pH of a fluoride containing
15 composition to at least 10 can reduce the etch rate of oxide to nearly zero. However, at high pH values (>10) metal corrosion and electrogalvanic corrosion of certain metals such as tungsten or titanium can occur. This problem has typically been addressed by adding multiple corrosion inhibitors. The addition of corrosion inhibitors has its drawbacks in that some corrosion inhibitors may
20 interfere with the removal of etch residues. It has been found that adjusting the pH of a fluoride containing composition within a range of from 7 to 9 would balance the effects of oxide etching and etching and corrosion of metals. To minimize or eliminate electrogalvanic corrosion of tungsten it is necessary to narrow the pH range even further to from 7 to about 8.4. By adding a buffer one
25 can maintain the pH within predetermined ranges for the fluoride containing compositions. Where metal corrosion or electrogalvanic corrosion is not a concern, the buffered pH range is from greater than 7.0 to about 11.0. Preferably, the range is from greater than 7.0 to about 9.0 In cases where sensitive metals are present the pH range is from greater than 7.0 to about 8.4.
30 The buffered fluoride containing compositions exhibit reduced pH drift and more consistent etch performance characteristics.

Compounds not normally thought of as useful in buffer solutions such as benzotriazole (BZT) and vanillin (4-hydroxy-3-methoxy benzaldehyde) are used in the present invention. BZT is not typically thought of as a buffer. BZT is best known for its ability to protect copper by forming an oxide-like passivation layer on exposed copper metal. BZT is also known for its ability to chelate with Cu^{2+} in basic solutions, thereby reducing the potential for Cu^{2+} redeposition on wafers. It has also been found that in the aqueous buffered fluoride containing compositions of the invention BZT also provides corrosion protection for exposed titanium.

BZT has a pK_a of 8.38 and the hydrogen on the nitrogen is acidic and can be removed in aqueous solutions. In the compositions of the present invention BZT functions both as a weak acid in the buffer and a corrosion inhibitor.

Webster defines a buffer as, "a substance capable in solution of neutralizing both acids and bases and thereby maintaining the original acidity or basicity of the solution." Skoog and West, Fundamentals of Analytical Chemistry 3rd Edition, state, "A buffer solution is defined as a solution that resists changes in pH as a result of...small additions of acids or bases. The most effective buffer solution contains large and approximately equal concentrations of a conjugate acid-base pair." Buffers are typically thought of as weak acids and the widest buffering range against either an acid or a base which is about one pH unit on either side of the pK_a of the weak acid group is achieved by having equimolar concentrations of the acid and the conjugate base;

$\text{HB} \rightleftharpoons \text{H}^+ + \text{B}^-$; $K_a = [\text{H}^+][\text{B}^-]/[\text{HB}]$, when $[\text{B}^-] = [\text{HB}]$, then $\text{pH} = \text{pK}_a$

The conjugate base pair is HB and B^- , where B^- is the conjugate base. One can also use a protonated base as the weak acid and achieve a buffered system;

$\text{BH}^+ \rightleftharpoons \text{H}^+ + \text{B}$, $K_a = [\text{H}^+][\text{B}]/[\text{BH}^+]$, when $[\text{B}] = [\text{BH}^+]$, then $\text{pH} = \text{pK}_a$

Here the conjugate acid base pair is BH^+ and B, where B is referred to as the conjugate base. Setting the pH is most easily accomplished by having an equimolar ratio of the acid and conjugate base for the acid (or protonated base) with the appropriate pK_a .

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The buffers of the present invention provide aqueous, fluoride containing compositions that exhibit little or no pH drift on standing overtime, when heated or when diluted with water in amounts up to 95% by weight of the total composition as opposed to unbuffered compositions. An example of pH drift in an unbuffered product over time is shown in Figure 1. The pH of an unbuffered product composed of dimethylacetamide (DMAC), deionized water, ammonium fluoride and ammonium hydroxide having a pH of 8.3 is monitored over time. As can be seen, the pH decreases from >8 to <4 over a period of seven days with the greatest change occurring within the first two days. The stability of the pH of a composition is important in stripping and cleaning operations because uniform performance characteristics are desirable and the etch rate and metallic corrosion of an unbuffered composition will vary as the pH changes on standing or during use.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1- A graph showing the change in pH on standing of an unbuffered, fluoride containing composition of the type typically used for stripping and cleaning operations.

Figure 2- A graph showing the change in pH on standing of a buffered, fluoride containing composition of the present invention.

Figure 3- A bar graph showing the decrease in pH of an unbuffered and two buffered samples on heating at 40°C for three hours.

Figure 4- A graph showing the change in TEOS etch rate of an unbuffered fluoride stripping/cleaning composition with changes in pH.

Figure 5- A bar graph showing the etch rates of various metals when exposed to an acidic fluoride containing composition and a buffered near neutral fluoride composition.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to aqueous, buffered fluoride containing compositions having a pH greater than 7.0 to about 11.0. The compositions are used as resist

and etch or ash residue removers and cleaners in the production of semiconductor devices. The aqueous, buffered, fluoride containing compositions have a pH greater than 7.0 to about 11.0 and comprise;

A. a fluoride containing compound of the general formula R_4NF where R is independently hydrogen, an alcohol group, an alkoxy group, an alkyl group or mixtures thereof, and

B. a buffer.

All weight percents are based on the total weight of the aqueous, buffered, fluoride containing composition.

Fluoride is an essential component of the present invention. Fluoride containing compounds include those of the general formula R_4NF where R is independently hydrogen, an alcohol group, an alkoxy group, an alkyl group and mixtures thereof. Examples of such compositions are ammonium fluoride, tetramethyl ammonium fluoride and tetraethyl ammonium fluoride. Fluoroboric acid can also be used as a fluoride containing composition. The fluoride containing compound or mixture of compounds is preferably present in amounts of from 0.1% by weight to 20% by weight based on the total weight of the composition.

The composition of the invention also includes a buffer. The pH of the composition is adjusted to a desired pH within a range of greater than 7.0 to about 11.0, preferably from greater than 7.0 to about 9.0, most preferably greater than 7.0 to 8.4. The buffer consists of a conjugate acid-base pair. The acid used is a weak acid or protonated base acting as the weak acid in solution. A variety of weak acids or protonated bases are readily available for buffers over a pH range of greater than 7.0 to 11.0. In addition compositions not normally thought of as useful buffers such as benzotriazole, selected biological compositions like glycine or vanillin and the like can be used. Methods of preparing buffers are well known in the art. The composition of the present invention can be buffered at a desired pH by adding the weak acid or protonated base and the conjugate base in requisite amounts. One can also prepare the buffer in situ by adding the weak acid or protonated base and a base in calculated amounts to the fluoride containing composition.

Examples of bases include amines, ammonia, alkylammonium hydroxides, ammonium hydroxide and the like.

Examples of weak acids and protonated bases that can be used in buffers around a pH of 7 or more are listed in Table 1.

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TABLE 1

Substance	pK _a
Abietic acid (Sylvic acid)	7.62
α -Alanine, methyl ester	7.74(+1)
2-Aminoacetamide	7.95(+1)
4-Amino-3-bromomethylpyridine	7.47(+1)
2-Aminobutanoic acid, methyl ester	7.64(+1)
1-Aminoisoquinoline	7.62(+1)
4-Aminoisoxazolidine-3-one	7.4(+1)
2-Amino-3-methylpyridine	7.24(+1)
2-Amino-4-methylpyridine	7.48(+1)
2-Amino-5-methylpyridine	7.22(+1)
2-Amino-6-methylpyridine	7.41(+1)
2-Aminoquinoline	7.34(+1)
Aspartic diamide	7.00
Aspidospermine	7.65
<i>N,N</i> -Bis(2-hydroxyethyl)-2-aminoethane sulfonic acid (BES)	7.15
<i>N-tert</i> -Butylaniline	7.10(+1)
4-Chloro-2-(2'-thiazolylazo)phenol	7.09
Chrome Dark Blue	7.65
Codeine	7.95(+1)
2-Cyanoethylamine	7.7(+1)
2-Cyclohexyl-2-pyrroline	7.91(+1)
Diacetylacetone	7.42
5,5-Diallylbarbituric acid	7.78
1,3-Dichloro-2,5-dihydroxybenzene	7.30
2,3-Dichlorophenol	7.44
2,3-Dichlorophenol	7.85
<i>N,N</i> -Diethyl- <i>o</i> -toluidine	7.18(+1)
Dihydroergonovine	7.38(+1)
3,4-Dihydroxybenzaldehyde	7.55
2,6-Dihydroxypurine	7.53
1,10-Dimethoxy-3,8-dimethyl-4,7-phenanthroline	7.21
<i>N,N'</i> -Dimethylethylenediamine- <i>N,N'</i> -diacetic acid	7.40
Dimethylhydroxytetracycline	7.5
2,6-Dimethyl-4-nitrophenol	7.19
<i>N,N'</i> -Dimethyl- <i>p</i> -toluidine	7.24(+1)
Emetine	7.36(+1)
Ergometrinine	7.32(+1)
Ethyl-2-mercaptoacetate	7.95
5-Ethyl-5-pentylbarbituric acid	7.96
5-Ethyl-5-phenylbarbituric acid	7.45

2-Ethyl-2-pyrrolone	7.87(+1)
N-Ethylveratramine	7.40(+1)
Glycine, ethyl ester	7.66(+1)
Glycine hydroxamic acid	7.10
Glycine, methyl ester	7.59(+1)
Glyoxaline	7.03(+1)
Harmine	7.61(+1)
Heroin	7.6(+1)
Hexamethyldisilazane	7.55
1,2,3,8,9,10-Hexamethyl-4,7-phenanthroline	7.26
4-Hydroxybenzaldehyde	7.62
4-Hydroxybenzonitrile (4-Cyanophenol)	7.95
10-Hydroxycodine	7.12
N-(2-Hydroxyethyl)piperazine-N'-ethansulfonic acid (HEPES)	7.55
5-Hydroxy-2-(hydroxymethyl)-4H-pyran-4-one	7.90
2-Hydroxy-3-methoxybenzaldehyde (o-vanillin)	7.91
4-Hydroxy-3-methoxybenzaldehyde (vanillin)	7.40
3-Hydroxy-4-nitrotoluene	7.41
Isopilocarpine	7.18(+1)
Leucine amide	7.80(+1)
Leucine, ethyl ester	7.57(+1)
Methoxycarbonylmethylamine	7.66(+1)
4-Methoxy-2-(2'-thiazoylazo)phenol	7.83
2,2'-Methylenebis(4-chlorophenol)	7.6
1-Methylimidazole	7.06(+1)
4-Methylimidazole	7.55(+1)
N-Methylmorpholine	7.13(+1)
4-(Methylsulfonyl)phenol	7.83
Methylthioglycolic acid	7.68
1-Methylxanthine	7.70
Morphine	7.87(+1)
3-(N-Morpholino)propanesulfonic acid (MOPS)	7.20
2-Nitrohydroquinone	7.63
2-Nitrophenol	7.22
4-Nitrophenol	7.15
2-Nitropropane (CS)	7.68
N-Pentylveratramine	7.28(+1)
Phenosulfonephthalein	7.9
3-Phenyl- α -alanine, methyl ester	7.05
N-Propylveratramine	7.20(+1)
Pyrocatecholsulfonephthalein	7.82
Serine, methyl ester	7.03(+1)
Solanine	7.34(+1)

Sylvic acid (Abietic acid)	7.62
2,3,5,6-Tetramethylpyridine	7.90(+1)
Thebaine	7.95(+1)
3-Thio-S-methylcarbide	7.56(+1)
1,3,5-Triazine-2,4,6-triol	7.20
2,4,5-Trichlorophenol (CS)	7.37
3,4,5-Trichlorophenol	7.84
Triethanolamine	7.76(+1)
2,3,6-Trimethylpyridine	7.60(+1)
2,4,6-Trimethylpyridine (2,4,6-Collidine)	7.43(+1)
Tris(2-hydroxyethyl)amine	7.76(+1)
2-[Tris(hydroxymethyl)methylamino]-1-ethansulfonic acid (TES)	7.50
Tyrosine amide	7.48
Tyrosine, ethyl ester	7.33
Uridine-5'-diphosphoric acid	7.16
L-Valine, methyl ester	7.49(+1)
Vetramine	7.49(+1)
Vitamine B ₁₂	7.64(+1)

+1 after the pK_a denotes that the acid is the protonated base; $BH^+ \rightleftharpoons B + H^+$, $K_a = [B][H^+]/[BH^+]$

The absence of a +1 after the pK_a denotes a normal acid dissociation; $BH \rightleftharpoons B^- + H^+$, $K_a = [B^-][H^+]/[BH]$

Examples of preferred weak acids includes HEPES, benzotriazole, and vanillin. Water is present in the buffered fluoride containing compositions. It can be present coincidentally as a component of other elements of the invention such as aqueous ammonium fluoride solution or an aqueous buffer solution, or it can be added separately. Water is present in amounts of from 1 % by weight to 92 % by weight, preferably water is present in amounts of from 1% to 70% by weight of the total composition. The presence of water improves the solubility of ammonium fluoride in the fluoride containing compositions of the invention as well as improving the ability to remove inorganic etch residues. In addition the aqueous, buffered, fluoride containing compositions can further contain an organic, polar solvent miscible in water. The organic polar solvents miscible in water are those solvents typically used in formulations for stripping and cleaning applications. Examples of acceptable organic polar solvents include a sulfoxide such as dimethylsulfoxide (DMSO), a sulfone such as dimethyl sulfone, an amine such as monoethanolamine (MEA), triethanolamine (TEA) or N-methyl ethanolamine (NMEA), an amide such as formamide or dimethylacetamide (DMAC), a lactone such as gamma-butyrolactone, a pyrrolidone such as N-methylpyrrolidone (NMP), an imidazolidinone such as 1,3-diethyl-2-imidazolidinone, a glycol such as polyethylene glycol (PEG) or ethylene glycol monobutyl ether and the like. DMAC is a preferred organic polar solvent. The organic polar solvent is preferably present in amounts up to 70% by weight based on the total weight of the composition. Other components such as corrosion inhibitors can be added to the aqueous, buffered fluoride containing compositions. If present the corrosion inhibitors are added in an amount up to 20% by weight of the total weight of the composition. Preferably the corrosion inhibitors are present in amounts of from 1% by weight to 5% by weight. Examples of suitable corrosion inhibitors includes benzotriazole, gallic acid, catechol, pyrogallol and esters of gallic acid. Benzotriazole functions both as an inhibitor and a weak acid in a buffer solution.

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The aqueous, buffered fluoride containing compositions are able to maintain their pH even after contamination with acidic or caustic media. Unlike unbuffered fluoride containing compositions that are subject to drifting pH, the buffered compositions of the present invention can maintain their pH related performance characteristics such as reduced oxide etch rate, reduced metallic and electrogalvanic corrosiveness and cleaning efficacy for longer periods of time. Having thus described the invention the following examples are provided for illustrative purposes and are not to be construed as limiting in nature. All amounts are given in weight percent unless otherwise noted. pH measurements are made on 5% aqueous solutions at room temperature. Metal etch rates were determined using a CDE ResMap 273 Four Point Probe (E-M-DGLAB-0007). 500 mls of test solution was placed in a 600 ml beaker with stirring and heated, if required to the specified temperature. If the metal to be tested was titanium an initial dip in phosphoric acid was required. The initial thickness of a wafer was determined using the CDE ResMap 273 Four Point Probe. After determining the initial thickness, test wafers were immersed in the test solution. If only one test wafer was being examined a dummy wafer was added to the solution. After five minutes the test wafers were removed from the test solution, rinsed for three minutes with deionized water and completely dried under nitrogen. If a negative stripper solution was used an intermediate rinse of the test wafer in a solvent such as DMAC or IPA (isopropyl alcohol) was performed for three minutes prior to the water wash. The thickness of each wafer was measured and if necessary the procedure was repeated on the test wafer. Oxide etch rates were determined using a Nanospec AFT 181 (E-M-DGLAB-0009). 200 mls of a test solution was placed in a 250 ml beaker with stirring and heated, if required, to the specified temperature. Three circles were scribed on each of the wafers to be tested. The marked areas on each wafer were the areas in which measurements would be taken. Initial measurements of each wafer were taken. After the initial measurements the wafers were immersed in the test solution for five minutes. If only one wafer was placed in a beaker containing solution a dummy wafer was placed in the beaker. After five minutes

each test wafer was washed with deionized water for three minutes and dried under nitrogen. If a negative stripper solution was used DMAC, IPA or another suitable solvent was used to rinse the test wafers for three minutes prior to the water rinse. Measurements of the scribed areas on each wafer were taken and if necessary the procedure was repeated.

Example 1

A buffered fluoride-containing composition was prepared using vanillin (4-hydroxy-3-methoxy benzaldehyde) and NH_4OH . Vanillin has a pK_a of 7.40. To ensure the concentration of the acid (vanillin) and the base are equal the molarity of NH_4OH was half the molarity of the acid. All the components were mixed in a vessel with stirring.

Component	Amount
DMAC	64.05
DI Water	28.90
Vanillin	4.00
NH_4OH (28% NH_3 sol)	0.80
NH_4F (40%sol)	1.25
Benzotriazole	1.00

The calculated pH for the solution was 7.39, the measured pH was 7.34.

Example 2

A solution was prepared in the same manner as Example 1

Component	Amount
DMAC	51.70
DI Water	35.00
Vanillin	4.00
NH_4OH (28% NH_3 sol)	0.80
NH_4F (40%sol)	7.50
Benzotriazole	1.00

The calculated pH for the solution was 7.28 and the measured pH was 7.19.

Example 3

The compositions of Examples 1 and 2 were heated in an open vessel for three hours at 40°C. The pH of each of the solutions changed by about 0.6 pH units.

Example 4

- 5 A solution was prepared in the same manner as in Example 1.

Component	Amount
DMAC	49.65
DI Water	35.00
HEPES	6.00
10 NH ₄ OH(28%NH ₃ sol)	0.85
NH ₄ F(40%sol)	7.50
Benzotriazole	1.00

The calculated pH value was 7.43. The measured pH value was 7.34.

Example 5

- 15 A solution was prepared in the same manner as Example 1.

Component	Amount
DMAC	62.00
DI Water	28.90
HEPES	6.00
20 NH ₄ OH(28%NH ₃ sol)	0.85
NH ₄ F(40%sol)	1.25
Benzotriazole	1.00

The calculated pH value was 7.48. The measured pH value was 7.51.

Example 6 Comparative(unbuffered)

- 25 A solution was prepared in the same manner as Example 1.

Component	Amount
DMAC	67.50
DI Water	30.00
NH ₄ OH(28%NH ₃ sol)	0.30
30 NH ₄ F(40%sol)	2.50

Additional ammonium hydroxide was added to raise the initial pH value to 8.3.

Example 7

The compositions of Examples 4 and 5 were allowed to set in open vessels at 25°C for seven days. During this time the pH values of the buffered compositions of examples 4 and 5 were monitored. The results are shown in Figure 2. The composition of Example 6 was treated in the same manner as Examples 4 and 5. The pH for the buffered samples remained relatively unchanged with a pH change of less than 0.25 pH units over the seven day period. By contrast, the unbuffered example had a pH change of greater than 4 pH units over the seven day period.

Example 8

Examples 4,5 and 6 were heated at 40°C for three hours and the pH values were determined. The results are shown in Fig. 3. The unbuffered composition had a decrease in pH value of more than 4 units, while buffered examples 4 and 5 had decreases in pH of no more than 1 unit.

Example 9

This example demonstrates how the oxide etch rate varies as a function of pH. For this procedure a weak base was added to adjust the pH upward to about 9.3. The pH was altered by diluting samples of the composition of example 6 so that the composition was 95% by weight of DI water. Oxide etch rates were determined optically on a Nanospec ATF using the standard procedure E-M-DGLAB-0009. The etch rate study was run with test wafers consisting of TEOS (tetraethyl ortho silicate) on silicon. Results are shown in Fig. 4.

Example 10

Differences in etch rates of various metals for Examples 5 and 6 were determined. The metals included Al/Cu(4%), Cu, Ti, W, Ta, TaN, TiN, TiW, undensified TEOS, densified TEOS, and thermal dioxide. Metal etch rates were determined using a CDE ResMap 273 and a standard procedure E-M-DGLAB-0007, CDE ResMap 273 Four Point Probe Etch Rate. Test wafers consisted of the appropriate metal on SiO₂ on silicon. Results are shown in Fig. 5.